

## AN ANGLE RESOLVED PHOTOELECTRON SPECTROMETER FOR ATOMS AND MOLECULES \*

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An angle resolved photoelectron spectrometer has been constructed and coupled to the high throughput 2 m normal incidence monochromator now in operation at SURF-II. The electron analyzer whose design has been previously reported [2] scans the angular distribution of the ejected photoelectrons in a plane perpendicular to the partially polarized exit beam from the monochromator. The intensity of the photon beam from the monochromator is monitored by measuring the photocurrent from a screen in front of a three mirror polarization analyzer which is used to determine the degree of polarization of the photon beam. The function of the spectrometer is under computer control which also acquires and processes the data output from the apparatus. Two novel features are employed to make the system highly effective: one is a capillary which channels the monochromatized output photon beam to the gas-photon-interaction zone and isolates the  $10^{-4}$  vacuum in the spectrometer chamber from the  $10^{-9}$  vacuum in the monochromator; the second feature is a high speed cryopump which permits a high density gas jet to interact with the photon beam while maintaining a high enough vacuum to minimize electron scattering and permit operation of the channeltron electron detector. These features combined with output fluxes of  $5 \times 10^{10}$  photons/s $^{-1}$  A $^{-1}$  permit vibrationally resolved photoelectron spectra of N $_2$  and CO to be obtained in about 15 min.

### 1. Introduction

Photoelectron spectroscopy, a field which has grown rapidly over the past few years, has become a standard technique in studies of band structure in solids, molecular structure and electron correlation effects in atoms and molecules. Now that an intense, polarized, continuum source, in the form of synchrotron radiation, has become more generally available, variable wavelength photoelectron angular and energy distribution measurements are adding a wealth of information in the above fields. Compared with a line

source such as the HeI resonance lamp, however, the intensity available at the exit slit of a monochromator mounted on a synchrotron radiation source has generally been one to two orders of magnitude lower. This deficiency has resulted in low resolution spectra in general, usually adequate for many solid state experiments, but generally inadequate for atomic and molecular spectroscopy. The new high flux normal incidence monochromator installed at the NBS Synchrotron Storage Ring, SURF II, has sufficient intensity and resolution to permit vibrationally resolved molecular spectra to be taken. The effects of auto-ionization, and other resonances in the ionization continuum of molecules, on the vibrational intensity distributions within the electronic bands can be studied. We describe here an electron spectrometer designed specifically for the SURF II monochromator [1], enabling measurements of both photoelectron

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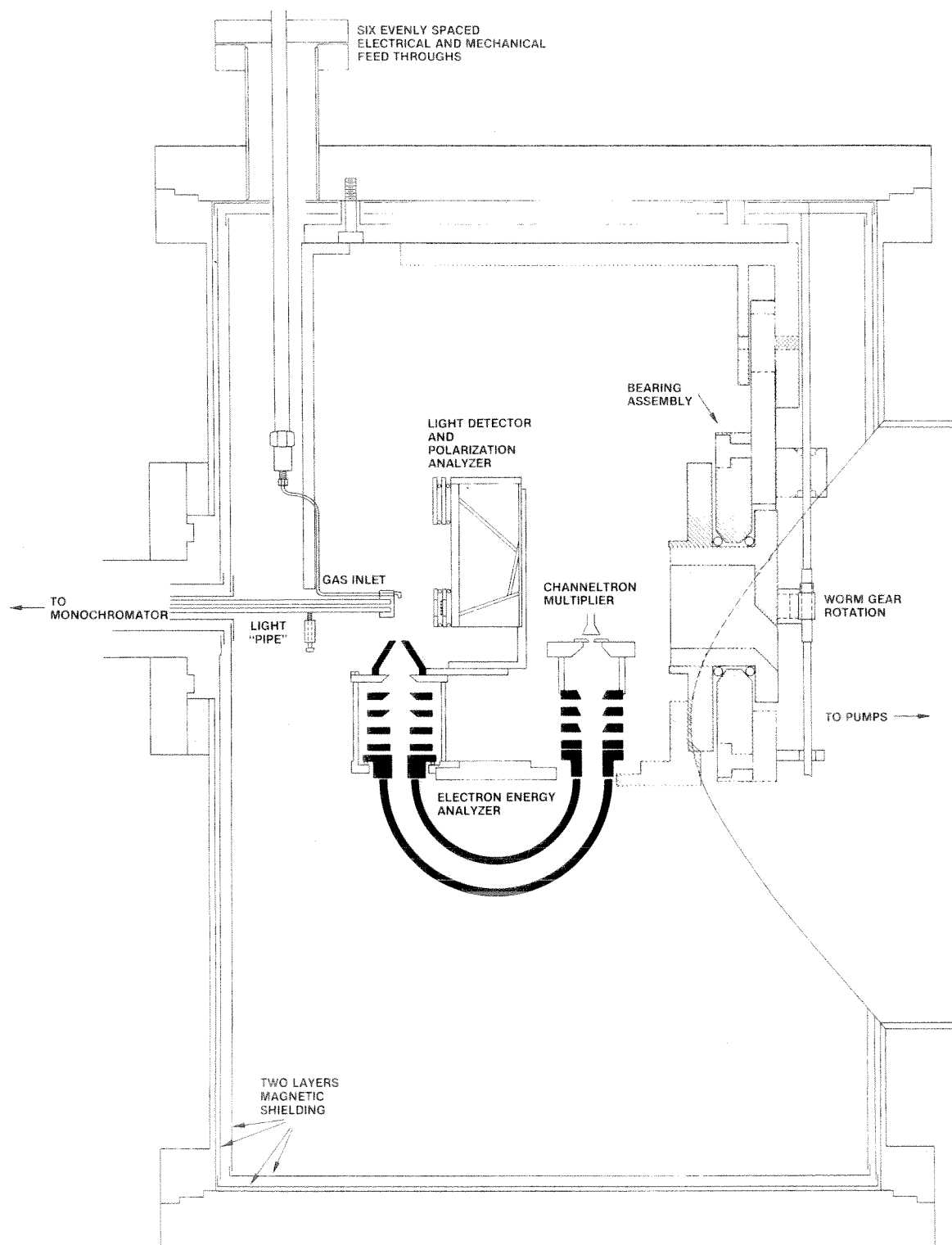


Fig. 1. Cross section drawing of electron energy analyser and associated mechanical components situated in the vacuum chamber. The main chamber has an inside diameter of 34.3 cm and a height of 51.5 cm. For clarity of presentation not all the details of the devices are shown on this diagram.

angular distribution and partial cross sections to be made in the photon energy range 5–35 eV.

## 2. The photoelectron spectrometer

The basis of the spectrometer is two copper hemispheres of 5 cm mean radius, with variable focal length lenses focusing the electron source onto a virtual entrance slit and onto the channeltron detector after energy analysis. This analyser has been described briefly elsewhere [2]. Fig. 1 shows the layout of the spectrometer in its vacuum chamber, which is shielded from external magnetic fields by two layers of annealed  $\mu$ -metal near the chamber walls inside the vacuum. The spectrometer rotates about an axis in the plane of fig. 1 coincident with the light beam direction, and is driven externally by a stepping motor. A 2 mm bore capillary-tubing light guide is used to channel the photons leaving the exit slit of the monochromator into the interaction zone. Prior measurements indicated that there were negligible losses in photon intensity by using this device and thus the geometric loss involved in having the interaction region of the electron spectrometer some distance from the exit slit of the monochromator was avoided. The capillary was also found to have a negligible effect on the polarization of the light leaving the monochromator.

The use of a  $1000\text{ l s}^{-1}$  closed cycle helium cryopump permitted a high density gas jet in the interaction region while still maintaining a vacuum of  $2 \times 10^{-4}$  Torr in the chamber. All materials inside the chamber were compatible with a clean vacuum and a base pressure of  $2 \times 10^{-8}$  Torr was routinely obtained without bakeout.

The polarization of the incoming light was measured by a three-mirror polarizer similar in principle and reflection angles to the device described by Horton et al. [3]. In the wavelength region of interest here, it has a rejection ratio of approximately 20 : 1 against the component perpendicular to the reflecting surface and is used as a polarization analyser. This analyser is shown on fig. 1 and rotates with the electron spectrometer. At its entrance a tungsten grid was placed to monitor the incoming photon flux, and at its exit a tungsten plate to monitor the beam after the three reflections. The gold coatings on the mirrors were connected to a +45 V battery to provide bias for the tungsten diodes. The resulting currents were measured by vibrating reed electrometers.

The alignment of the electron spectrometer with the light beam emerging from the monochromator was a critical procedure. First of all, the capillary was aligned to the monochromator photon beam. The electron spectrometer was then adjusted, without disturbing the capillary so that its rotation axis coincided with the light beam. The gas jet was then aligned to the capillary by visual inspection.

The correctness of this procedure was tested using a laboratory HeI resonance lamp. Since this is an unpolarized light source, the electron count rate should be the same at any spectrometer angle and this was found to be the case within five percent, using the argon  $^2\text{P}_{1/2,3/2}$  doublet. The peak count rate at a resolution of 100 mV, and the helium source running at 200 mA, was  $\sim 3000\text{ s}^{-1}$ . By reducing the pass energy from 5 to 2 V a resolution  $\sim 35\text{ mV}$  was obtained using  $1\frac{1}{2}\text{ mm}$  apertures on the analyser.

## 3. The data acquisition system

The experiment runs under computer control and is based on a CAMAC system interfaced with an LSI-11 computer stationed in the CAMAC crate. Fig. 2 shows the salient features of the system. The computer drives the monochromator to the desired wavelength, then sets the electron analyser angle with respect to the  $E$  vector of the incidence radiation. The user chooses these initial parameters as well as setting the voltage range over which the electron spectrometer will scan. The electron pass energy through the analyser is kept constant and the voltage ramp is superimposed on a preset retarding potential, thereby maintaining constant energy resolution. A second channel on the ramp generator (CAMAC power supply controller) is used to control the focus potential on the entrance lens of the analyser, which has to be varied with incident electron kinetic energy. The computer program scans the electron spectrometer repetitively over the voltage range, adding each scan to the previous one, until a pre-selected maximum electron count in any one voltage channel is reached. The data are then stored on a floppy disc drive, plotted on an  $X$ – $Y$  plotter, the analyser moved to the next angular position and the scanning cycle repeated. The multiple scan technique avoids the effects of long term drifts in gas jet pressure, channeltron gain, etc. The electron counts are referenced to the photon flux at each voltage using the tungsten mesh photodiode. Through the voltage to frequency

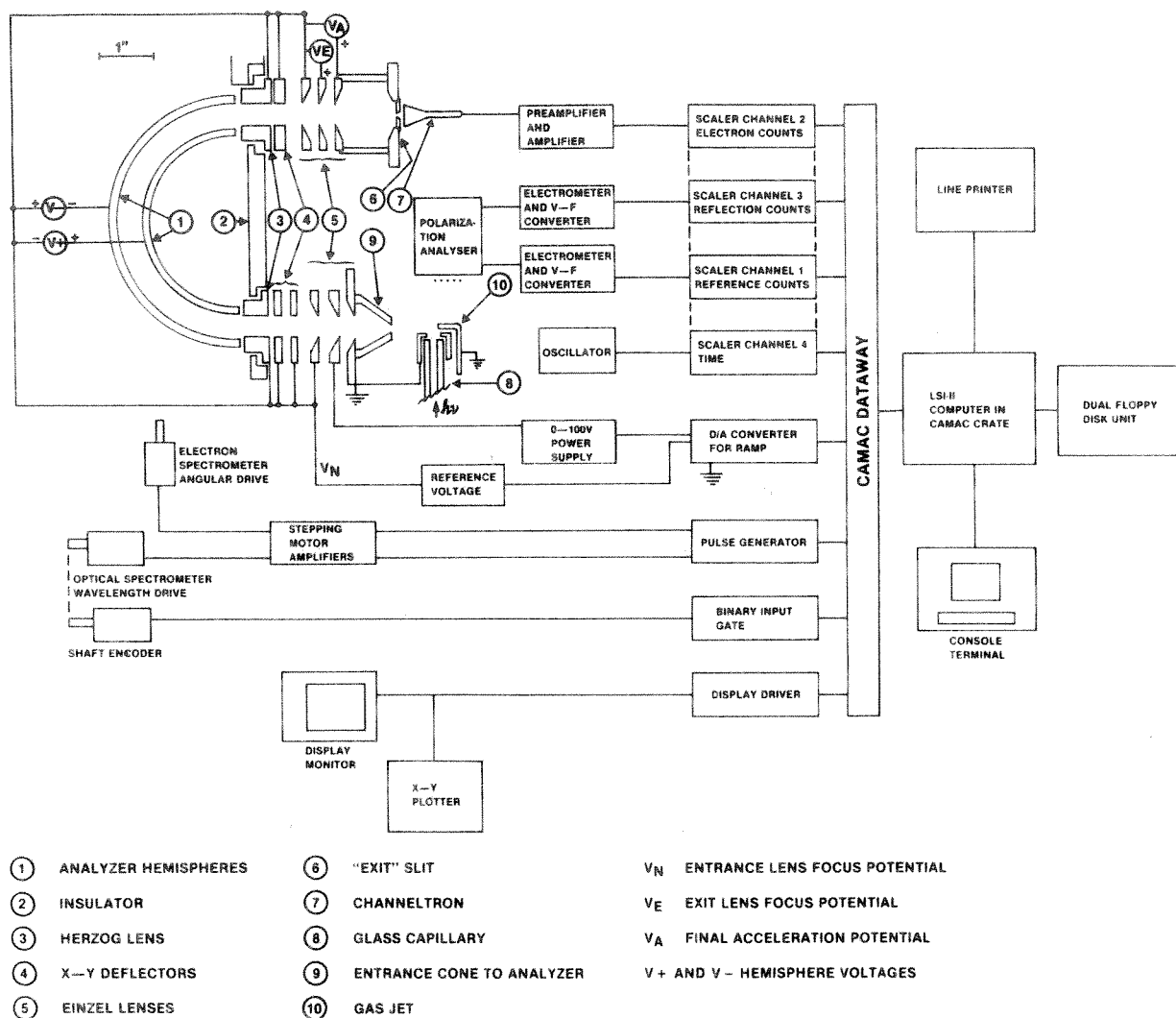


Fig. 2. Schematic diagram of electron spectrometer data acquisition and control system.

converter this signal is fed to the input of one of the scaler channels, which inhibits the counting process after a preset count is reached. The data ramp voltage, electron count, photon intensity count, polarization analyser reflected count, and time are then stored and the spectrometer repositioned at the next angle. Typically each voltage scan takes between 1 and 5 min (i.e., a peak count of  $\sim 1000 \text{ s}^{-1}$ ), the total number of scans depending on sample cross section and photon intensity. The system also provides facilities via a CAMAC module to interrupt the program in a controlled way, giving the user a choice of continuing the present run, terminating it and storing the data or abandoning the present run.

#### 4. The experimental data

The differential cross section for a particular photoionization channel is given by

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \{1 + \beta[3p \cos(2\Theta) + 1]/4\}.$$

Thus a knowledge of the polarization

$$p = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

of the incident light is required and is measured by comparing the ratios of the direct and reflected signals in the polarization analyzer when it is set

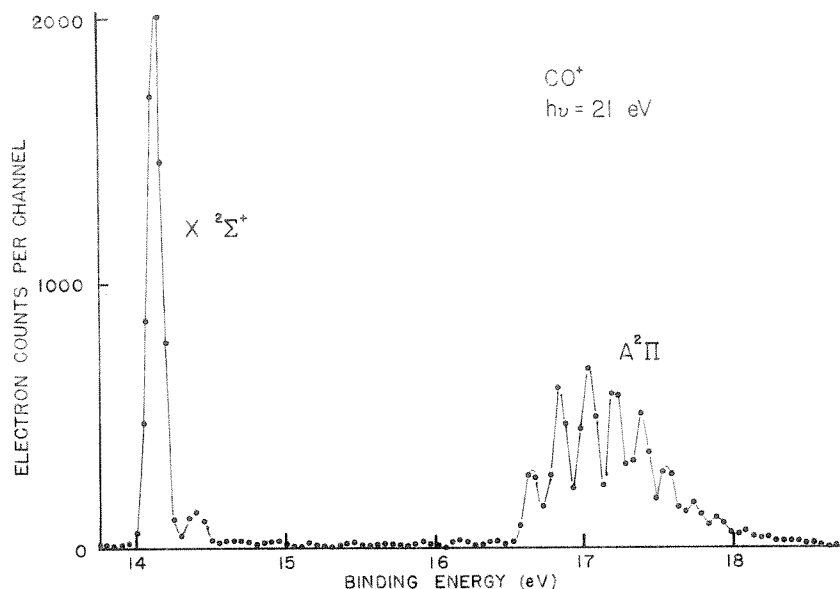


Fig. 3. Photoelectron spectrum of CO with photons of 21 eV energy. The horizontal axis is the binding energy of the electron in eV and the vertical axis is total electron counts per channel.

along the  $E$  vector and perpendicular to it. In the above expression  $\Theta$  is the direction of the ejected electron with respect to the electric vector and  $\sigma$  the partial cross section for that channel,  $\beta$  is the asymmetry parameter.  $I_{\parallel}$  and  $I_{\perp}$  are the photon intensities whose electric vectors are parallel and perpendicular respectively to the major polarization axis. The above expression is readily deduced from the equations in Samson and Gardner [4].

The first measurements made with this analyser were branching ratios of molecular vibrational levels. To do this an angle had to be chosen such that the data were independent of  $\beta$ . The polarization of the light at the exit slit has been measured at  $h\nu = 20$  eV and found to be equal to  $0.75 \pm 0.05$  and thus at  $\Theta = 58^\circ$  the dependence of  $d\sigma/d\Omega$  on  $\beta$  vanishes. The uncertainty in  $p$  caused uncertainties in this value of  $\Theta$  less than the angular acceptance of the electron spectrometer ( $\sim 3^\circ$ ). Fig. 3 shows a carbon monoxide spectrum taken at 21 eV using a 5 eV pass energy in the electron spectrometer. The total scan took 15 min with a combined resolution of monochromator and electron spectrometer of 110 mV. There is considerable interest in the branching ratios of the vibrational peaks associated with the  $^2\Sigma^+$  ground state of

$\text{CO}^+$ , especially in the region around 22 eV where a shape resonance in the  $5\sigma$  channel is predicted theoretically. A similar resonance is predicted in the  $3\sigma$  channel in  $\text{N}_2$  by Dehmer and Dill [5] and measurements on these two molecules to map out and identify these resonances will be reported in the near future, as well as studies of the effects of auto-ionizing resonances on Franck-Condon distributions.

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